

SYNTHESES OF SOME SUBSTITUTED
COUMARANONES

BY

JOHN ANDERSON

A.B., Georgetown College, 1934

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1938

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INTRODUCTION

Coumaran-3-ones condense readily with aromatic aldehydes to give 2-benzalcoumaran-3-ones¹ and these arylidene coumaranones are readily hydrogenated to give the corresponding 2-benzylcoumaran-3-ones². This leads to a simple synthesis of 2-benzylcoumaran-3-ones. It seems reasonable that similar condensations involving aliphatic aldehydes and ketones should take place, providing favorable experimental conditions could be found, and thus lead to a simple general synthesis of 2-alkylcoumaran-3-ones which heretofore have been prepared only by ring closure of *o*-hydroxy-*w*-haloacetophenones³. The object of this work was the realization of this possibility through the study of the condensation of simple aldehydes and ketones with 6-methoxycoumaran-3-one.

Complete reduction of 2-alkylcoumaran-3-ones leads to 2-alkylcoumarans which are of especial interest because such ring systems constitute a portion of the rotenone molecule.

EXPERIMENTAL

In glacial acetic acid solution, with hydrochloric acid as the condensing agent, 6-methoxycoumaran-3-one combined with ketones to give 2,2'-bis-(6-methoxycoumaran-3-one)-dialkylmethanes. Three ketones were used, acetone, ethyl methyl ketone and diethyl ketone. A similar condensation took place, in methanol solution, between the coumaranone and formaldehyde, acetaldehyde, propionaldehyde and *n*-butraldehyde, providing a zinc chloride-hydrochloric acid mixture was used as the condensing agent.

In absolute ethanol, in the presence of zinc chloride, 6-methoxycoumaran-3-one combined with acetone in a one-to-one ratio to yield 2-isopropylidene-6-methoxycoumaran-3-one. Cyclohexanone gave a similar product but the higher aliphatic ketones did not condense under these conditions.

2-Isopropylidene-6-methoxycoumaran-3-one was reduced catalytically to 2-isopropyl-6-methoxycoumaran-3-one with hydrogen and platinum catalyst. With palladium deposited on Norite

as the catalyst, reduction both of the double bond and of the ketone group took place, resulting in the formation of 2-isopropyl-6-methoxycoumaran. The reduction of the isopropylidene derivative to the isopropylcoumaranone offers a new method for the synthesis of 2-alkylcoumaran-3-ones and complete reduction to the 2-isopropylcoumaran constitutes a simple synthesis of this type of molecule.

Acetylation of 6-methoxycoumaran-3-one with acetic anhydride gave the acetyl derivative of the enol form. That this compound was the O-acetyl derivative was shown (a) by acid hydrolysis to regenerate the parent coumaranone and (b) by catalytic reduction to 3-acetoxy-6-methoxydihydrobenzofuran which lost acetic acid to produce 6-methoxybenzofuran.

SUMMARY

Aliphatic aldehydes and ketones condensed with 6-methoxycoumaran-3-one to give 2,2'-bis-(6-methoxycoumaran-3-one)-alkylmethanes. In the case of acetone and cyclohexanone, condensation also was effected in a one-to-one ratio to yield alkylidene coumaranones.

Catalytic reduction of the alkylidene coumaranones with platinum and hydrogen yielded the 2-alkyl-6-methoxycoumaran-3-ones. With a palladium catalyst the reduction of 2-isopropylidene-6-methoxycoumaran-3-one to 2-isopropyl-6-methoxycoumaran was accomplished.

A compound obtained by the action of acetic anhydride on 6-methoxycoumaran-3-one has been shown to be the acetyl derivative of the enol form of the coumaranone.

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VITA

The author was born in Prestonpans, Scotland, on July 15, 1910. He received his elementary education in the schools of that city and graduated from Prestonpans Public School in July, 1924. He entered Georgetown College (Georgetown, Kentucky) in the fall of 1930 and received the A.B. degree in June, 1934. The following September he entered the graduate school of the University of Florida as a Graduate Scholar and remained in residence in that institution for two years. In the fall of 1936 he entered the graduate school of the University of Illinois and since that time he has held the appointment of Assistant in Chemistry.



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